

PATENT SPECIFICATION

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NO DRAWINGS

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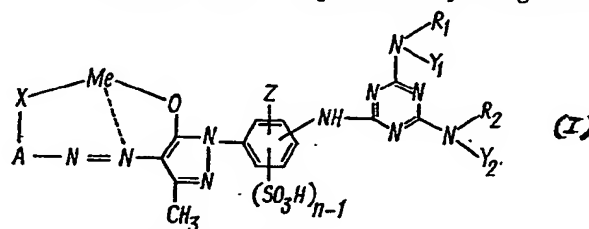


(54) METALLISED MONOAZO DYESTUFFS AND PROCESSES FOR THEIR MANUFACTURE

(71) We, CIBA-GEIGY A.G. a Swiss Body Corporate of Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides new metallised monoazo dyestuffs, processes for their manufacture, their use for dyeing material containing collagen, especially leather, and organic material, and the material dyed by using the new dyestuffs. The dyestuffs possess good fastness properties, especially high fastness to light, as well as good levelling capacity and affinity.

The dyestuffs of the invention may be represented by the general formula



in which A represents an optionally substituted radical of the benzene or naphthalene series, X represents —O— or —COO— in the o-position to the azo bond, Z represents hydrogen, halogen or a lower alkyl, lower alkoxy or carboxyl group, R₁ represents hydrogen or a lower alkyl group, R₂ represents hydrogen or an aliphatic radical, Y₁ represents a radical of the benzene or naphthalene series which optionally contains sulphonic acid groups, Y₂ represents an aliphatic, cycloaliphatic or aromatic radical, n is 1 or 2 and Me represents copper, nickel or iron, the dyestuff containing a total of at least 2 and at most 5 sulphonic acid groups per molecule.

The term "lower" used throughout this specification means "containing up to 4 carbon atoms".

The substituents on the benzene or naphthalene radicals A may be, for example, alkyl groups with 1 to 3 carbon atoms, alkoxy groups with 1 to 3 carbon atoms, halogen atoms, nitro, carbacylamino, lower alkylsulphonyl, sulphamoyl, N-mono-substituted or N,N-disubstituted sulphamoyl or sulphonic acid groups, for example methyl, ethyl, n-propyl, isopropyl, methoxy, ethoxy, propoxy, chlorine, bromine, fluorine, acetylamino, chloromethylsulphonylamino, benzylamino, methylsulphonyl, ethylsulphonyl, methylaminosulphonyl, ethylaminosulphonyl, dimethylaminosulphonyl and diethylaminosulphonyl.

When Y₂ or R₂ represents an aliphatic radical, it is preferably a saturated or unsaturated alkyl radical with 1 to 18 carbon atoms, which may be unsubstituted or substituted by, for example, hydroxyl groups, lower alkoxy groups, the nitrile group, halogen atoms, such as chlorine or bromine, carboxyl groups or sulphonic acid groups. As Examples of suitable aliphatic radicals are methyl, ethyl, n-propyl, isopropyl,

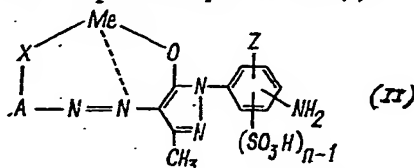
n-butyl, isobutyl, sec. butyl, tert. butyl, pentyl, isopentyl, hexyl, heptyl, octyl, decyl, dodecyl, stearyl, vinyl, allyl, oleyl, β -hydroxyethyl, β -chloroethyl, β -cyanoethyl, α,β -dihydroxyethyl, β -ethoxyethyl, carboxymethyl and sulphoethyl.

If Y_2 represents a cycloaliphatic radical, it is preferably cyclopropyl, cyclohexyl, cycloheptyl or cyclododecyl. If Y_2 represents an aromatic radical, it preferably belongs to the benzene series and can possess customary ring substituents, for example halogens, such as fluorine, chlorine or bromine, and lower alkyl, lower alkoxy or sulphonic acid groups.

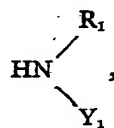
When Y_1 represents a radical of the benzene series, it can contain up to 2 sulphonic acid groups, and when it denotes a radical of the naphthalene series it can contain up to 3 sulphonic acid groups.

The dyestuffs of Formula I can be manufactured by several processes.

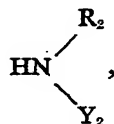
For example, the metallised monoazo dyestuffs may be obtained by reacting a cyanuric halide stepwise and in optional sequence with (a) a compound of formula II:



in which A, X, Z, Me and n are as defined above, (b) an amine of formula



and (c) an amine of formula



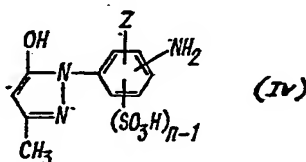
in which R_1 , Y_1 , R_2 and Y_2 are as defined above, the molar ratio of the reactants being 1:1:1:1.

The starting substances used are known or can easily be manufactured according to known processes.

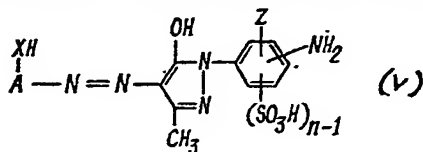
For example, a compound of Formula II is obtained if the diazonium compound of an amine of Formula III:



in which A and X are as defined above is coupled in the usual manner with a coupling component of Formula IV:



in which Z and n are as defined above to give an azo compound of Formula V:



in which A, X, Z and n are as defined above and the latter compound is treated with a metal-donating agent to give the compound of formula II.

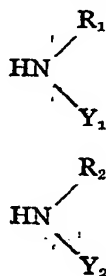
The metal-donating agents may be the customary, preferably water-soluble, simple or complex salts of the metals represented by Me with organic or inorganic acids. Preferably the water-soluble nickel salts, iron salts and especially copper salts of mineral acids or lower fatty acids are used.

Examples of suitable metal-donating agents are copper-II sulphate, copper-II acetate, nickel-II sulphate, nickel-II acetate, nickel-II chloride, iron-II sulphate, iron-III sulphate or ammoniacal copper salt solutions.

Examples of suitable amines of Formula III are 2-aminophenol-3-, -4- and -6-sulphonic acid, 2-aminophenol-4,6-, -3,4-, -3,5- and -3,6-disulphonic acid, 2-amino-6-acetylamino- and -6-benzylaminophenol-4-sulphonic acid, 2-amino-4-acetylamino- and -4-benzylamino-phenol-6-sulphonic acid, 2-amino-3-acetyl-amino-phenol-5-sulphonic acid, 2-amino-5-acetylamino- and -5-priopionylamino-phenol-3-sulphonic acid, 2-amino-6-nitrophenol-4-sulphonic acid, 2-amino-5-nitrophenol-3-sulphonic acid, 2-amino-6-chloro-, -6-bromo- and -6-fluoro-phenol-4-sulphonic acid, 2-amino-4-chloro- or -4-bromo-phenol-6-sulphonic acid, 2-amino-6-methyl-, -6-ethyl-, -6-n-propyl-, -6-isopropyl- and -6-butyl-phenol-4-sulphonic acid, 2-amino-4-methyl-, -4-ethyl- and -4-propyl-phenol-6-sulphonic acid, 2-amino-3-methyl- and -3-propyl-phenol-5-sulphonic acid, 2-amino-5-methyl- and -5-propyl-phenol-3-sulphonic acid, 2-amino-3-methoxy-, -3-ethoxy- and -5-propoxy-phenol-5-sulphonic acid, 2-amino-5-methoxy-, -5-ethoxy and -5-propoxy-phenol-3-sulphonic acid, 2-amino-4-methoxy-, -4-ethoxy- and -4-propoxy-phenol-6-sulphonic acid, 2-amino-6-methoxy-, -6-ethoxy- and -6-propoxy-phenol-4-sulphonic acid, 2-amino-3-, -4-, -5- and -6-sulphamoylphenol, 2-amino-3-, -4-, -5- and -6-dimethylaminosulphamoylphenol, 2-amino-5-diethylaminosulphamoylphenol, 2-amino-3- and -5-methylaminosulphamoylphenol, 2-amino-6-nitro-4-methylsulphonylphenol, 2-amino-5-nitro-3- and -4-ethylsulphonyl- or -4-propylsulphonylphenol, 2-amino-4-methylsulphonyl-, -4-ethylsulphonyl-, -4-propylsulphonylphenol-6-sulphonic acid, 2-amino-6-methylsulphonyl and -6-ethylsulphonyl-phenol-4-sulphonic acid, 2-amino-3-methylsulphonylphenol-5-sulphonic acid, 2-amino-5-methylsulphonylphenol-3-sulphonic acid, 2-amino-1-carboxybenzene-3-, -4-, -5- and -6-sulphonic acid, 2-amino-1-carboxybenzene-4,6- and -3,5-disulphonic acid, 2-amino-6-chloro-1-carboxybenzene-5-sulphonic acid, 2-amino-6-methyl-1-carboxybenzene-4-sulphonic acid, 2-amino-4-nitro-1-carboxybenzene-6-sulphonic acid, 2-amino-4-acetylamino-1-carboxybenzene-5-sulphonic acid, 2-amino-3-methoxy-carboxybenzene-5-sulphonic acid, 2-amino-4-methylsulphonyl-1-carboxybenzene-6-sulphonic acid, 2-amino-5-sulphamoylbenzoic acid, 1-aminonaphthol-(2)-4- and -6-sulphonic acid, 1-amino-6-nitronaphthol-(2)-4-sulphonic acid, 1-aminonaphthol-(2)-4,6-disulphonic acid and 2-aminonaphthol-(1)-4-sulphonic acid or -4,6-disulphonic acid.

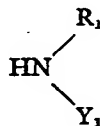
Examples of suitable coupling components of Formula IV are: 1-(3'- and 4'-aminophenyl)-3-methylpyrazolone-(5), 1-(3'- and 4'-aminophenyl-6'-sulphonic acid)-3-methylpyrazolone-(5), 1-(3'- and 4'-aminophenyl-5'-sulphonic acid)-3-methylpyrazolone-(5), 1-(4'-amino-5'- and -6'-methoxyphenyl)-3-methylpyrazolone-(5), 1-(3'-amino-5'- and -6'-methoxyphenyl)-3-methylpyrazolone-(5), 1-(4'-amino-5'- and -6'-methyl- or ethyl-phenyl)-3-methylpyrazolone-(5), 1-(3'-amino-2'-methyl-phenyl-5'-sulphonic acid)-3-methylpyrazolone-(5), 1-(4'-amino-2'- and -3'-methylphenyl-6'-sulphonic acid)-3-methylpyrazolone-(5), 1-(4'-amino-2'- and -3'-fluoro-, -chloro- or -bromo-phenyl)-3-methylpyrazolone-(5) and 1-(3'-amino-5' and -6'-chloro- or -bromo-phenyl)-3-methylpyrazolone-(5).

The stepwise condensation of a compound of Formula II with cyanuric halide and the amines of the formulae



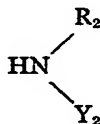
may be carried out in a known manner, appropriately in an aqueous medium, optionally in the presence of an inert, easily removable, organic solvent, such as a lower aliphatic ketone, for example acetone, and preferably in the presence of agents which buffer mineral acids, such as sodium carbonate or potassium carbonate, sodium hydroxide or potassium hydroxide, disodium or trisodium phosphate or dipotassium or tripotassium phosphate, sodium acetate or potassium acetate or sodium metasilicate.

Examples of suitable amines of the formula



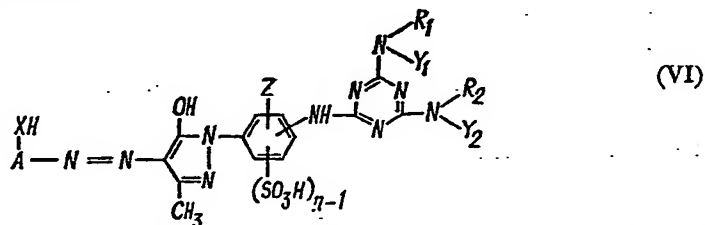
are 1-aminobenzene-2-, -3- or -4-sulphonic acid, 1-aminobenzene-2,6-, -2,3- and -2,4-disulphonic acid, N-methyl-, N-ethyl-, N-propyl-, N-butyl-N-phenylamine, 1-methylaminobenzene-4-sulphonic acid, 1-methylaminobenzene-2,4- and -2,5-disulphonic acid, 1-ethylamino- and 1-propylamino-benzene-4-sulphonic acid, 1-ethylaminobenzene-2,4-disulphonic acid, 1-aminonaphthalene-3,6-disulphonic acid, 1-aminonaphthalene-3- and -6-sulphonic acid, 2-aminonaphthalene-4- and -8-sulphonic acid or 2-aminonaphthalene-4,8-disulphonic acid.

Examples of suitable amines of the formula

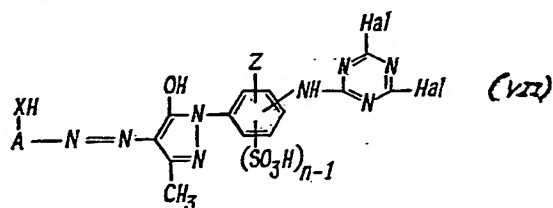


are methylamine, dimethylamine, ethylamine, diethylamine, propylamine, dipropylamine, isopropylamine, di-isopropylamine, di-n-butylamine, sec. butylamine, tert. butylamine, pentylamine, dipentylamine, hexylamine, dihexylamine, heptylamine, diheptylamine, octylamine, dioctylamine, decylamine, didecylamine, dodecylamine, stearylamine, distearylamine, N-methyl-N-butylamine, N-methyl-N-ethylamine, N-methyl-N-octylamine, N-methyl-N-stearylamine, N-ethyl-N-octylamine, N-ethyl-N-stearylamine, phenylamine, 4-methyl-, 4-ethyl- or 4-propyl-phenylamine, phenylamine-4-sulphonic acid, N-methyl- and N-ethyl-N-phenylamine, N-methyl-N-4-methyl-phenylamine, N-methyl-N-cyclohexylamine, N-methyl-N-cyclopropylamine, N-methyl-N-cycloheptylamine, cyclododecylamine, N-methyl-N-cyclododecylamine, cyclohexylamine, cycloheptylamine, methoxymethylamine, ethoxymethylamine, γ -isooctoxy-n-propylamine, β -ethoxy-ethylamine, β -methoxy-ethylamine, β -hydroxyethylamine, di(β -hydroxy)-ethylamine, 2-aminoethylsulphonic acid, vinylamine, divinylamine, allylamine, diallylamine, oleylamine and dioleylamine.

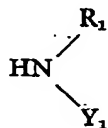
Metallised monoazo dyestuffs of Formula I can also be manufactured by treating a compound of Formula VI:



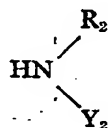
in which A, X, Z, R₁, R₂, Y₁, Y₂ and n are as defined above with an agent which donates the metal Me. The compound of formula VI may be prepared by reacting a compound of Formula VII:



in which A, X, Z and n are as defined above and Hal represents halogen, in optional sequence with amines of the formulae



and



in which R_1 , Y_1 , R_2 and Y_2 are as defined above.

The condensation and metallisation in this latter process can be carried out as described above.

The metallised monoazo dyestuffs of the invention can be salted out from their solution or suspension (preferably after neutralisation) by means of an alkali metal salt, such as sodium chloride or potassium chloride, filtered off, washed with aqueous sodium chloride solution or potassium chloride solution and appropriately dried at elevated temperature and, if desired, under reduced pressure.

The dyestuffs of Formula I are red to brown powders. They are soluble in water and resistant to boiling-down, and are suitable for dyeing material containing collagen, such as leather, especially re-tanned leather, chrome-tanned suede leather or grain leather. They show a good levelling capacity and give level dyeings particularly on re-tanned leather.

The leather can be dyed in the usual manner in an aqueous dyeing liquor which is weakly acid, for example containing formic acid, with vigorous agitation. Leather dyeings obtained with the dyestuffs of Formula I are distinguished by good fastness to light, by good depth dyeing of the leather and by uniform colour shades of good covering power, which only change slightly on buffing suede leather. Moreover, when leather, dyed according to the invention, is treated with rubber or plasticised polymers, for example polyvinyl chloride, of a different colour, as, for example, in shoe production, no diffusion of the dyestuffs of the invention into the rubber or into the polymer occurs.

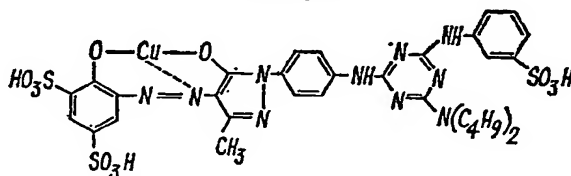
Spray dyeing or wash dyeing of dried leather with the dyestuffs according to the invention is also possible and gives good fastness properties.

Suitable organic materials which can be dyed or printed with the dyestuffs according to the invention are above all natural and synthetic polyamide fibres.

The dyestuffs of Formula I in which A represents an optionally substituted radical of the benzene series, X represents $-O-$, Z and R_1 represent hydrogen, R_2 represents an optionally substituted lower alkyl group, especially an n-butyl group, Y_1 represents a sulphophenyl radical, Y_2 represents an aliphatic radical, especially an n-butyl radical, n is 1, and Me represents copper, are of particular importance, since they have particularly good fastness to light and good levelling capacity and affinity.

The Examples which follow illustrate the invention.

Example 1.



26.9 g of 2-amino-phenol-4,6-disulphonic acid are diazotised in the usual manner and coupled, at 10—20°C and pH 9, with 18.9 g of p-aminophenylmethylpyrazolone. The dyestuff is converted into the copper complex by adding 25 g of crystalline copper sulphate as a 25% solution, at pH 8—9. The dyestuff solution thus obtained is added dropwise over the course of 30 minutes, at 0—5°C, to an aqueous suspension of 18.4 g of cyanuric chloride, and the pH value is maintained at between 7 and 8 by simultaneous addition of aqueous sodium hydroxide solution. After completion of

- the condensation, 17.3 g of metanilic acid in the solid form are introduced into the reaction solution whilst it is still cold. The reaction mixture is then warmed to 35—40°C and condensed for 3 hours at pH 8—9, whilst adding aqueous sodium hydroxide solution. When the condensation of metanilic acid is complete (this can be ascertained chromatographically) the reaction mixture is treated with 12.9 g of n-dibutylamine, warmed to 90°C and condensed for one hour at pH 9—10, with occasional addition of aqueous sodium hydroxide solution. The dyestuff of the above formula is precipitated from the reaction mixture, whilst the latter is still hot, by adding sodium chloride, and is filtered off hot and washed with concentrated sodium chloride solution. After drying in vacuo, it is a brown powder and dyes leather in pure, brown shades. The dyeing on leather is distinguished by very good fastness to light and additionally the leather is dyed to a good depth.
- Dyestuffs with similar properties are obtained if instead of the compounds quoted in Example 1 equivalent amounts of the components quoted in Table I below are used, and in other respects the procedure according to Example 1 is followed.
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|----|--|----|
| 5 | | 5 |
| 10 | | 10 |
| 15 | | 15 |

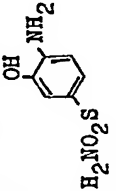
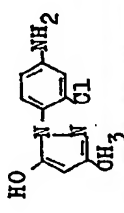
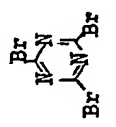
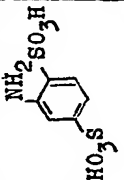
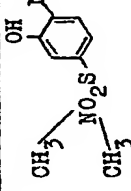
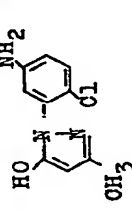
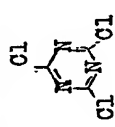
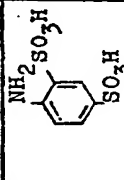
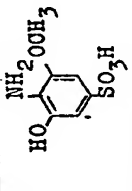
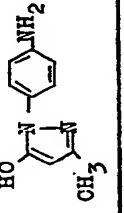
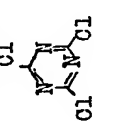
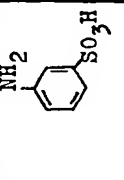
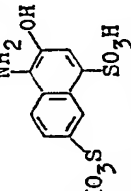
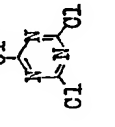
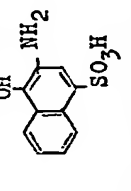
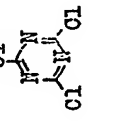
Example No.	Diazo Component	Coupling Component	Metal	Cyanuric Compound	1-Amine	2-Amine	Colour Shade on leather
6			Cu				Brown
7		"	Cu	"		"	Brown
8		"	Cu	"	"	"	Brown
9		"	Cu	"			Brown
10	"	"	Cu	"	"		Brown

Example No.	Diazo Component	Coupling Component	Metal	Cyanuric Compound	1-Amine	2-Amine	Colour Shade on leather
11			Cu				Brown
12	"	"	Cu	"	"		Brown
13			Cu	"	"		Yellowish brown
14		"	Cu	"			Yellowish brown
15			Cu	"			Yellowish brown

Example No.	Diazo Component	Coupling Component	Metal	Cyanuric Compound	1-Amine	2-Amine	Colour Shade on leather
16			Cu				Yellowish brown
17		"	Cu	"		"	Brown
18	"		Cu	"			Brown
19			Cu	"			Brown
20			Cu	"			Brown

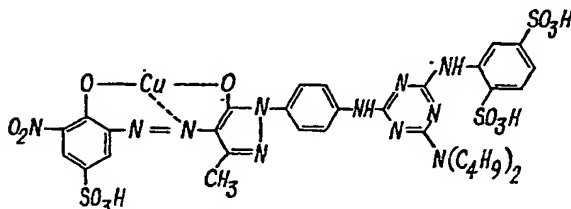
Example No.	Diazo Component	Coupling Component	Metal	Cyanuric Compound	1-Amine	2-Amine	Colour Shade on leather
21			Cu			$C_8H_{17}NH_2$	Brown
22			Cu			$C_4H_9-NH_2$	Brown
23			Cu			$(C_{18}H_{37})_2NH$	Brown
24			Cu			$(C_{18}H_{37})_2NH$	Brown

Example No.	Diazo Component	Coupling Component	Metal	Cyanuric Compound	1-Amine	2-Amine	Colour Shade on leather
25			Cu			$\text{C}_2\text{H}_5\text{NH}_2$	Brown
26			Cu			$(\text{CH}_3)_2\text{CHOH}_2\text{NH}_2$	Brown
27			Cu			$\text{C}_{18}\text{H}_{37}\text{NH}_2$	Brown
28			Cu			$(\text{C}_4\text{H}_9)_2\text{NH}$	Brown

Example No.	Diazo Component	Coupling Component	Metal	Cyanuric Compound	1-Amine	2-Amine	Colour Shade on leather
29			Cu			$\text{H}_2\text{NCH}_2\text{CH}_2\text{SO}_3\text{H}$	Brown
30			Cu			$\text{C}_4\text{H}_9\text{NH}_2$	Brown
31			Cu			$(\text{C}_4\text{H}_9)_2\text{NH}$	Brown
32		"	Cu		"	$(\text{C}_4\text{H}_9)_2\text{NH}$	Brown
33		"	Cu		"	$(\text{C}_4\text{H}_9)_2\text{NH}$	Brown

Example No.	Diazo Component	Coupling Component	Metal	Oyanuric Compound	1-Amine	2-Amine	Colour Shade on leather
34			Cu				Brown
35			Cu		"		Brown
36		"	Cu		"		Brown

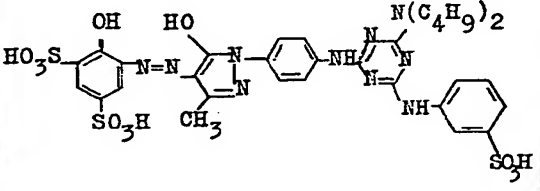
Example 37.



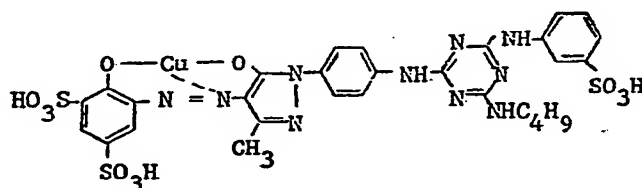
23.4 g of 6-nitro-2-aminophenol-4-sulphonic acid are diazotised and coupled with 18.9 g of p-aminophenylmethylpyrazolone under customary conditions. The dyestuff solution thus obtained is added dropwise, at 0—5°C and pH 6—7, to an aqueous suspension of 18.4 g of cyanuric chloride, with simultaneous addition of dilute aqueous sodium hydroxide solution in order to maintain the pH. After completion of the reaction, 25.3 g of aniline-2,5-disulphonic acid are added to the reaction mixture, the temperature is gradually raised to 50—60°C, and condensation is carried out for 4 hours at pH 8, whilst adding aqueous sodium hydroxide solution. 12.9 g of n-dibutylamine are added in order to replace the third halogen atom in the cyanuric radical. The reaction mixture is then warmed to 90°C and the pH is maintained at 9—10 by adding aqueous sodium hydroxide solution. After completion of the condensation, the dyestuff is precipitated by adding sodium chloride, filtered off and washed with sodium chloride solution. The press cake, whilst still moist, is dissolved in water at 80°C and 25 g of crystalline copper sulphate in the form of a 25% aqueous solution are added to the hot reaction mixture at pH 5. The copper complex dyestuff of the above formula is separated out completely by adding sodium chloride, filtered off, washed with sodium chloride solution and dried *in vacuo* at 90°C. It is a dark brown powder which dyes leather in reddish brown shades of very good fastness to light. The leather is furthermore dyed to a good depth.

Dyestuffs with similar properties are obtained if the procedure according to Example 37 is followed, but the dyestuffs listed in Table II below, column 2, are used and treated with equivalent amounts of the metal salts listed in column 3 instead of with 25 g of crystalline copper sulphate.

Table II

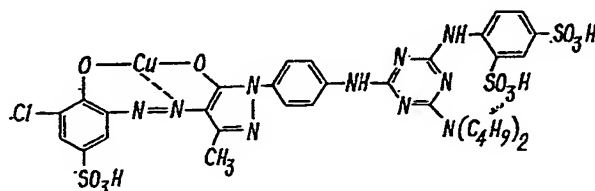
No.	Dyestuff	Metal salt	Colour shade on leather
38		$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	Reddish yellow
39	"	FeCl_3	Olive

Example 40



26.9 g of 2-aminophenol-4,6-disulphonic acid are diazotised at 0—5°C and coupled with 18.9 g of p-aminophenylmethylpyrazolone at 10—20°C. 32.1 g of 2-m-sulphophenylamino - 4,6 - dichloro - s - triazine, dissolved in 400 ml of water, are added dropwise over the course of 30 minutes to this dyestuff solution, at 35—40°C, and the pH is kept at 6—7 by simultaneous addition of aqueous sodium hydroxide solution, until the reaction is complete. 12.9 g of n-butylamine are then added to the reaction mixture, the temperature is raised to 90—95°C, and condensation is carried out for 2 hours at a pH of 9. After completion of the condensation, copper is introduced by adding 25 g of crystalline copper sulphate in a 25% solution in the presence of acetate ions, and thereafter the dyestuff is isolated and washed. After drying, the resulting brown powder dyes leather in brown shades.

Example 41.



The dyestuff obtained by diazotisation of 22.3 g of 6-chloro-2-aminophenol-4-sulphonic acid and coupling with 18.9 g of p-aminophenylmethylpyrazolone is converted into the corresponding copper complex dyestuff by means of copper sulphate in accordance with the instructions of Example 1. The dyestuff solution thus obtained is condensed, at 90—100°C and pH 7—8, with 49.5 g of the secondary condensation product, manufactured in a known manner, of 1/10 mol of cyanuric chloride, 1/10

mol of aniline-2,4-disulphonic acid and 1/10 mol of n-dibutylamine. After completion of the condensation, the dyestuff of the above formula is completely precipitated by adding sodium chloride, filtered off, washed with a sodium chloride solution and subsequently dried in vacuo at 90°C. It is a brown powder and dyes leather in brown shades.

Example 42.

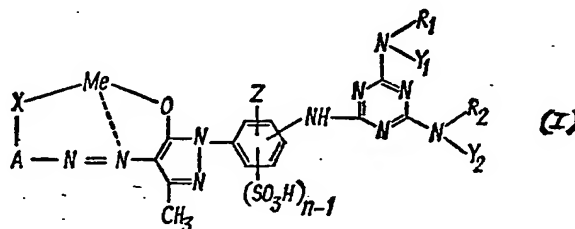
100 g of dry chrome-tanned suede leather are resoftened in the usual manner and beaten in 800 ml of water with 8 g of the dyestuff of Example 40 for 1 hour at 50°C. After this time, 4 g of 85% formic acid are added and the leather is beaten for a further 30 minutes. The leather dyed in this way is dried and finished in the usual manner. A dyeing of good fastness properties, especially good fastness to light and to buffing, is thus obtained.

Example 43.

100 g of shaved chrome leather is rinsed in running water at 30°C. It is then beaten for 45 minutes in a dyeing vat with 300 g of water at 30°C and 1 g of sodium bicarbonate. The leather pretreated in this way is then beaten for 20 minutes with 200 g of water at 50°C and 0.8 g of dyestuff of Example 1, and is greased in the usual manner with 3 g of a medium-sulphonated neat's foot oil in the same bath for 45 minutes. The leather is then dried and finished in the usual manner. A level, muted dyeing of good fastness properties, especially a high fastness to light, is obtained.

WHAT WE CLAIM IS:—

1. A dyestuff of formula

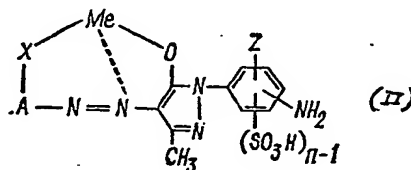


in which A represents an optionally substituted radical of the benzene or naphthalene series, X represents —O— or —COO— in the o-position to the azo bond, Z represents hydrogen, halogen or a lower alkyl, lower alkoxy or carboxyl group, R₁ represents hydrogen or a lower alkyl group, R₂ represents hydrogen or an aliphatic radical, Y₁ represents a radical of the benzene or naphthalene series which optionally contains sulphonate groups, Y₂ represents an aliphatic, cycloaliphatic or aromatic radical, n is 1 or 2 and Me represents copper, nickel or iron, the dyestuff containing a total of at least 2 and at most 5 sulphonate groups per molecule.

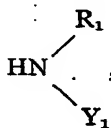
2. A dyestuff according to Claim 1, in which A represents an optionally substituted radical of the benzene series, X represents —O—, Z and R₁ represent hydrogen, R₂ represents an optionally substituted lower alkyl group, Y₁ represents a sulphonyl radical and Y₂ represents an aliphatic radical.

3. A dyestuff according to Claim 2, in which R₂ and Y₂ each represents an n-butyl radical, n is 1 and Me represents copper.

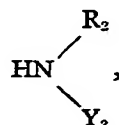
4. A process for the manufacture of a dyestuff according to Claim 1, which comprises reacting a cyanuric halide stepwise and in optional sequence, with (a) a compound of formula



in which A, X, Z, Me and n are as defined in Claim 1, (b) an amine of formula

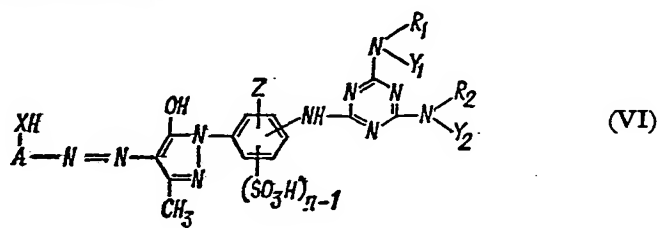


in which R_1 and Y_1 are as defined in Claim 1, and (c) an amine of formula



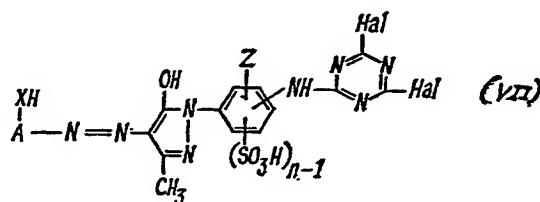
in which R_2 and Y_2 are as defined in Claim 1, the molar ratio of the reactants being 1:1:1:1.

5 5. A process for the manufacture of a dyestuff according to Claim 1, which comprises treating a compound of formula



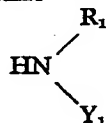
in which A, X, Z, R_1 , R_2 , Y_1 , Y_2 and n are as defined in Claim 1, with an agent which donates the metal Me.

10 6. A process for the manufacture of a dyestuff according to Claim 1 which comprises reacting a compound of formula:



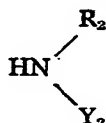
in which A, X, Z and n are as defined in Claim 1 and Hal represents halogen, in optional sequence with amines of formulae

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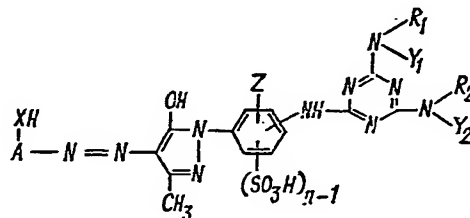
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and



in which R_1 , Y_1 , R_2 and Y_2 are as defined in claim 1, and treating the resulting compound of formula:

20



20

with an agent which donates the metal Me.

7. A process according to Claim 5 or 6, wherein the agent which donates the metal Me is copper-II sulphate, copper-II acetate, nickel-II sulphate, nickel-II acetate, nickel-II chloride, iron-II sulphate, iron-III sulphate or an ammoniacal copper salt solution.
- 5 8. A process according to any one of Claims 4 to 7 substantially as hereinbefore described. 5
9. A process according to Claim 4, substantially as described in any one of Examples 1 to 36 and 41.
- 10 10. A process according to Claim 6 substantially as described in any one of Examples 37 to 40. 10
11. A dyestuff according to Claim 1, whenever obtained by a process according to any one of Claims 4 to 10.
12. A dyestuff according to Claim 1 substantially as hereinbefore described.
- 15 13. A process for dyeing material containing collagen which comprises treating the material with a dyestuff according to any one of Claims 1 to 3, 11 and 12. 15
14. A process according to Claim 13, wherein the material containing collagen is leather.
15. Material containing collagen whenever dyed by a process according to Claim 13 or 14.

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